Crystals at High Pressure

X-ray studies of crystals compressed between a pair of gem-quality diamonds reveal a range of responses to increased pressure. Changes in atomic structure are best viewed in terms of polyhedral geometry

by Robert M. Hazen and Larry W. Finger

What happens to the atomic structure of a crystal when the external pressure is increased? In the broadest sense the answer is obvious: the individual atoms move closer together, reducing the crystal's volume. It is only in the past few years, however, that investigators have begun to analyze in detail the various ways in which compression affects particular arrangements of atoms. The gain in understanding has come from the marriage of two experimental tools. One, the diamond-anvil high-pressure cell, is a fairly recent addition to the laboratory; the other, the X-ray diffractometer, has been a mainstay of crystallographic research for decades.

The advent of the diamond-anvil cell has made it possible to achieve extraordinarily high pressures with unprecedented ease. Pressures in excess of two million atmospheres (equivalent to those near the core of the earth) can now be produced routinely at the interface of two small, gem-quality diamonds that are squeezed together

in a mechanically levered device similar to a nutcracker [see "The Diamond-Anvil High-Pressure Cell," by A. Jayaraman; SCIENTIFIC AMERICAN, April, 1984].

The tremendous pressure generated in a diamond-anvil cell can be transmitted to a single crystal hydrostatically (that is, uniformly in all directions) by immersing the crystal in a fluid that is confined by a metal gasket between the diamonds. Because diamonds are transparent to X-radiation, a narrow beam of X rays can be focused on the crystal, and the diffracted components of the beam can be measured by standard X-ray detection equipment. Thus the arrangement of the atoms in a crystal under high pressure can be determined in much the same way as it can in a crystal at atmospheric pressure.

Knowledge of the properties of matter at high pressure is crucial to understanding the earth's interior. Accordingly most of the several dozen compounds that have been studied to date with the new high-pressure crystallographic techniques have been miner-

als. Among them are oxides, silicates, halides and simple molecular crystals. At pressures comparable to those in the earth's lower mantle and core such minerals are reduced in volume by 50 percent or more. What changes in atomic structure can account for such a large loss of volume? What do these changes reveal about the nature of the forces between atoms?

The atomic bonding of most rock-forming minerals can be described in terms of a simple ionic model. Positively charged metallic ions, called cations, are typically surrounded by negatively charged ions, called anions. The cluster formed by a cation and its surrounding anions is usually quite regular in shape, with the anions (most commonly oxygen) corresponding to the corners of a tetrahedron, an octahedron, a cube or some other simple polyhedral form [see illustration below].

The representation of ionic clusters as cation-centered polyhedrons simplifies the description of complex crystal structures. Arrangements of many different atoms, which are difficult
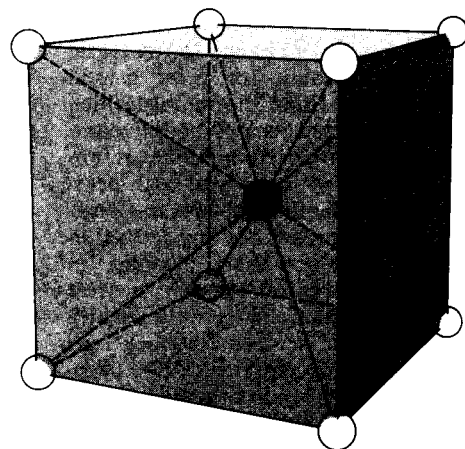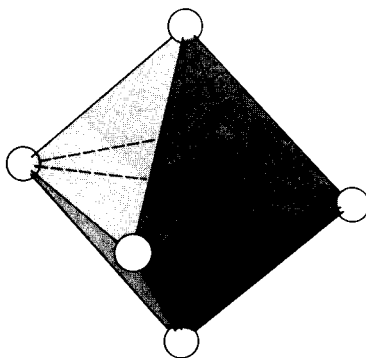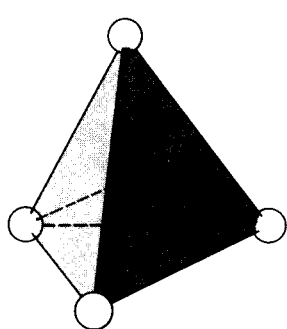
REGULAR GEOMETRIC CLUSTERS of negatively charged anions (*white*) surround a central, positively charged metallic cation (*color*) in many crystalline substances, including most common rock-forming minerals. Ionic compounds of this kind can be conveniently represented as arrays of polyhedrons; at the center of each polyhedron is a cation and at the corners are the anions. Three representative ionic structures are illustrated. In the rest of the polyhedral diagrams accompanying this article the ions are omitted.

to depict if every atom is shown, are reduced to simple geometric forms. Common binary compounds, such as the oxide of a single metal, can be represented by the packing of one type of polyhedron. Silicates and multiple-metal oxides can be similarly treated, although they call for two or more types of polyhedron.

Cation-centered polyhedrons are more than just visual aids. Each type of polyhedron has its own distinctive set of properties, which can be helpful in predicting the behavior of the bulk crystal. The recognition of the importance of these characteristic properties has led to a new approach to the modeling of different forms of solid matter. In this approach, called the polyhedral method, one first identifies the constituent polyhedrons and their properties; one then sums these factors for the bulk crystal. The procedure is often complex and depends to a large extent on how the polyhedrons are linked. In general two polyhedrons can be joined by a shared corner (that is, a single common anion), a shared edge (two common anions) or a shared face (three or more common anions). Alternatively two polyhedrons can be joined by weak molecular forces, in which case no anions are shared. The bulk properties of the crystal depend on the types of constituent polyhedrons and the nature of their linkages.

The polyhedral approach has been particularly effective for studying the behavior of crystals under compression. Each type of cation-centered polyhedron has its own value of compressibility, and the relations between the polyhedral linkages and the compressibility of the bulk crystal are comparatively straightforward. In order to predict how a particular crystal will behave under compression it is first necessary to understand the kinds of change pressure can impose on an atomic structure.

Three kinds of change in structural geometry account for most crystal compression. Bond shortening, which can be modeled as polyhedral compression in ionic compounds, is observed in all substances at high pressure and is therefore always responsible, at least in part, for any reduction in volume. Bond-angle bending, in which the distances between "nearest neighbor" atoms change only slightly while "second-nearest neighbor" atoms move much closer together, dominates compression in crystals in which the atoms are not densely packed. Intermolecular compression is the principal response to increased pressure in condensed molecular substances. Any combination of these three kinds of
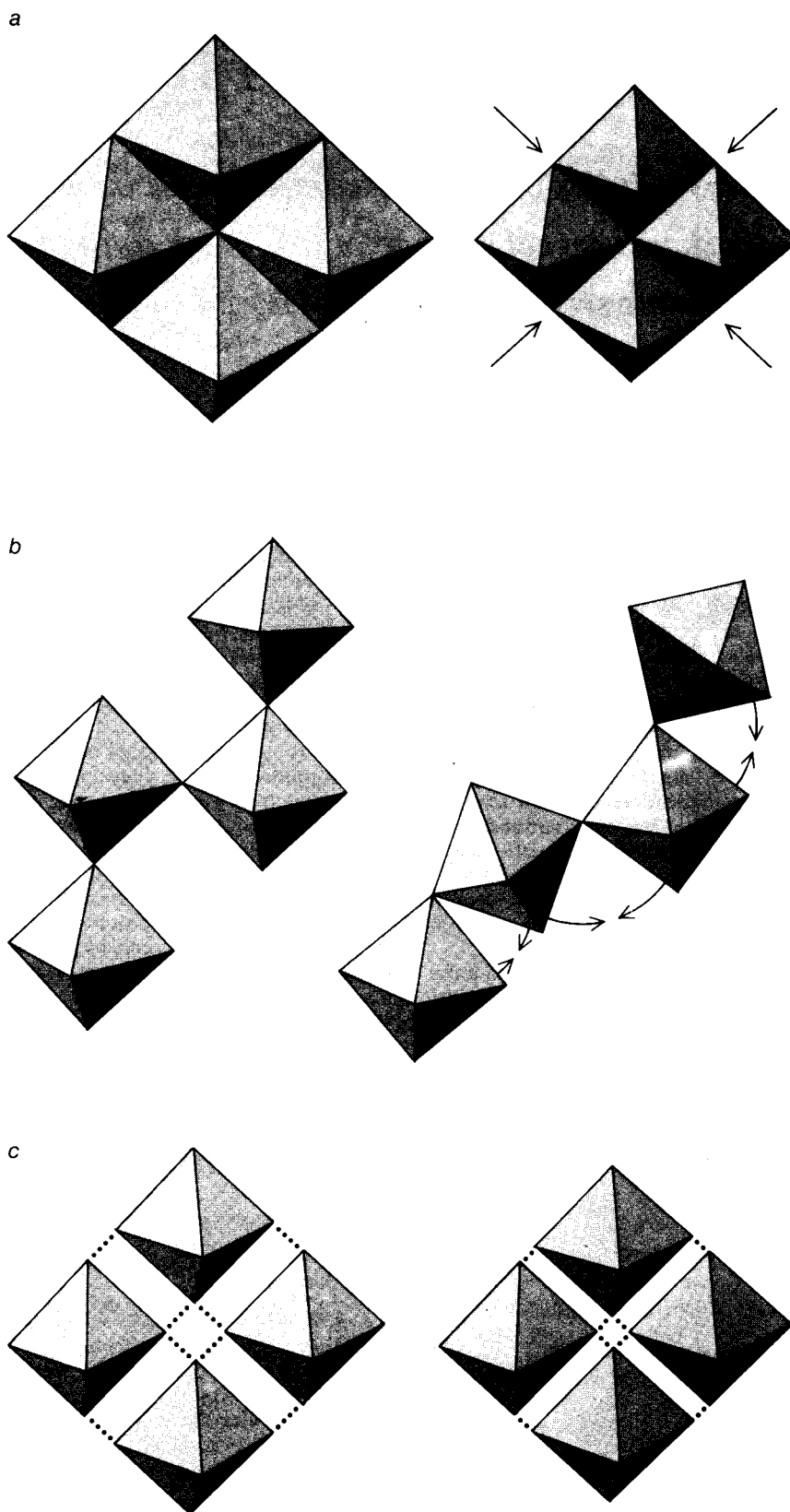
THREE POSSIBLE RESPONSES of a crystal structure to compression are shown in these polyhedral diagrams of typical atomic arrangements. Bond shortening (*a*) reduces the average distance between pairs of atoms. Bond-angle bending (*b*) changes the angles between adjacent bonds without significantly altering the length of the bonds. Intermolecular compression (*c*) is characteristic of solids that are made up of discrete molecules held together by weak bonds (*dotted lines*). Each of the three mechanisms shown reduces the volume of the bulk crystal by decreasing the average distance between the atoms; the magnitude of the changes and the final relative positions of the atoms, however, are different in each case.

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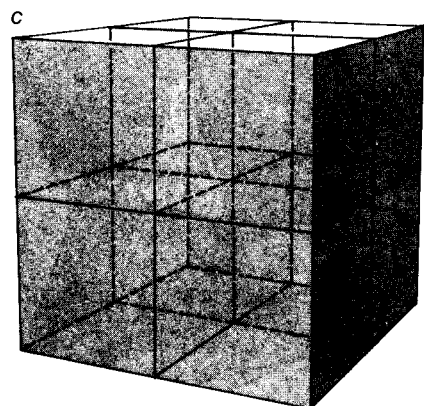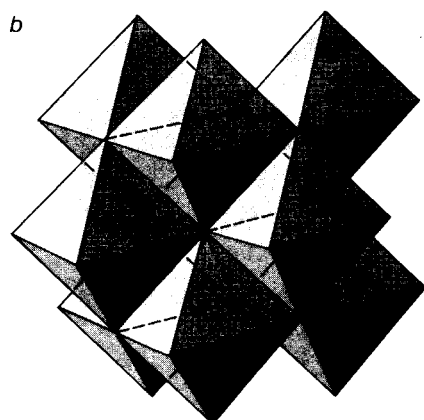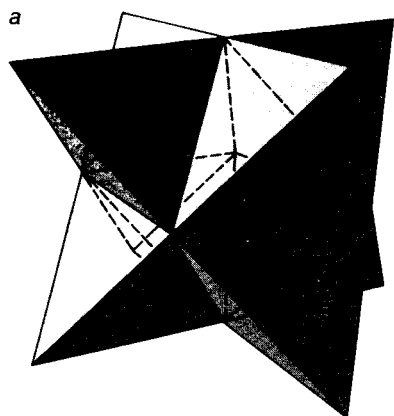
SIMPLE BINARY COMPOUNDS have structures that can be represented by a single type of cation-centered polyhedron. The compressibility of such crystals is uniform in all directions and is identical with the compressibility of the individual polyhedrons. In lithium oxide (*a*) each of the lithium cations is surrounded by a tetrahedron of oxygen anions. Sodium chloride (*b*) is composed of an edge-sharing array of sodium-centered octahedrons. Cesium chloride (*c*) consists of a face-sharing array of cubes.

geometric change can contribute to crystal compression.

Although bond shortening is observed in every compressed crystal, the magnitude of the shortening varies for different polyhedrons. Thus some cation-anion clusters in a given structure can be considered "soft," in the sense that they vary significantly in size according to the pressure, whereas others can be considered "hard," in that they show little change in size even at pressures as high as thousands of atmospheres. The range of compressibility from the most compressible bond to the least compressible one is more than 100 to one. In modeling crystal compression it is essential to know the relative compressibilities of the bonds that form the polyhedral clusters.

In spite of the wide range of observed bond compressibilities it is remarkable that any given type of polyhedron—a magnesium cation bonded to six oxygen anions, for example—displays very nearly the same compressibility in all crystals. A value of compressibility that is almost constant from structure to structure can therefore be assigned to each type of polyhedron. What factors govern the relative magnitudes of polyhedral compressibility, and how can these values be predicted?

Ionic bonds, which link cations and anions in the polyhedral cluster, can be described by a few simple parameters, including the length of the bond, the number of nearest neighbors of each ion and the electrostatic charge of both the cation and the anion. Linus Pauling, in his classic monograph *The Nature of the Chemical Bond*, successfully related many subtle features of crystals to these simple variables. We have taken the same approach in modeling polyhedral compression.

Two significant empirical relations have been found between the bonding parameters and the compressibility of a given polyhedron. First, polyhedral compressibility tends to be proportional to the cube of the distance between the ions and hence (roughly) to the volume of the polyhedron. Large polyhedrons, such as those of alkali cations, are more compressible than small polyhedrons, such as those of silicon or aluminum cations. It follows that the polyhedrons responsible for most of the volume of a crystal usually contribute most to crystal compression. Second, polyhedral compressibility is inversely proportional to the charge of the cations and the anions; hence the distance between cation-anion pairs with the strongest electrostatic interaction will be least affected by pressure. These two relations, which

were derived from the analysis of hundreds of measurements of bond compressibility, facilitate the prediction of bond and polyhedral compressibilities in oxides and silicates.

Bond shortening dominates compression in structures in which all polyhedrons are joined to adjacent polyhedrons by shared edges or faces. In these structures there are no discrete molecules for intermolecular compression, and bond-angle bending cannot occur without severe polyhedral distortions, which are not observed. Thus knowledge of the magnitude of polyhedral compression is sufficient to predict the behavior of these crystals under compression.

Simple binary compounds such as lithium oxide, sodium chloride and cesium chloride are among the easiest polyhedral structures to model at high pressure [*see illustration on this page*]. In each of these crystals the bulk compressibility is identical with that of the constituent polyhedrons; a measurement of the macroscopic change in volume with pressure corresponds to a direct measurement of polyhedral compression. When pressure is applied to such structures, it tends to decrease the distance between atoms without resulting in any significant change in the relative positions of the atoms.

Binary oxides, which have two kinds of cation-anion cluster, often exhibit more complex behavior. Scheelite-type compounds, which have the general chemical formula ABO_4 (in which the arbitrary symbols AB stand for some combination of metallic ions), are particularly interesting because of the great variety of AB cation pairs that are observed to form this structure [*see illustration on opposite page*]. As a rule the compressibility of a scheelite is determined by the compressibility of the large A polyhedron, which in turn depends on the electrostatic charge on the A cation.

Differential polyhedral compressibilities can lead to highly anisotropic, or direction-dependent, behavior in some crystals under pressure. For example, olivine, a common rock-forming mineral with the formula Mg_2SiO_4, has an array of magnesium-centered octahedrons that fill space in much the same way as the octahedrons do in the sodium chloride structure. In olivine, however, rigid silicon-centered tetrahedrons share edges with the octahedrons in one plane of the structure. As a result the compressibility of olivine in this plane is only about half the value observed in the unconstrained perpendicular direction. The small, rigid, silicon-centered polyhedrons, even though they account for

only a small fraction of the volume, have an important influence on the bulk properties of the mineral.

In all the examples considered above the polyhedrons share edges or faces; no bond-angle bending is observed in these structures. If the poly-hedrons in a structure share corners, the volume of the crystal is often reduced by changing the angles between the polyhedrons rather than by significantly shortening the ionic bonds within them. The ubiquitous mineral qua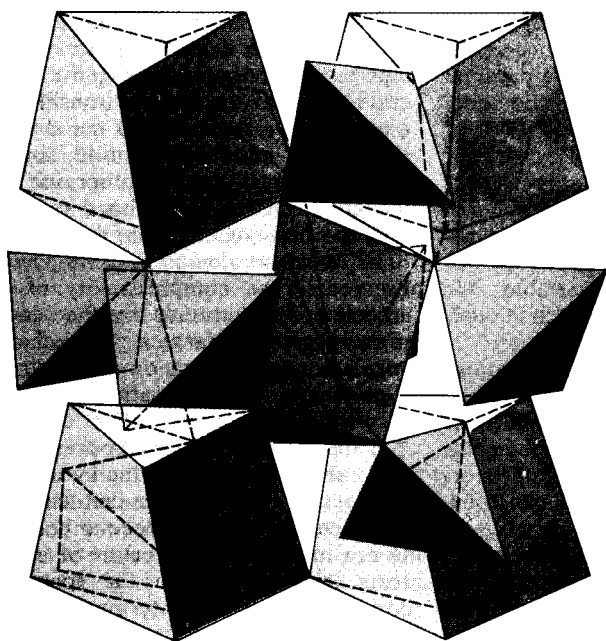rtz, the commonest oxide of sili-con, is perhaps the best-known example of this phenomenon [*see illustration on next page*]. The basic building blocks of the quartz structure are silicon-centered tetrahedrons, each of which shares four corners with four other tetrahedrons to form a contin-
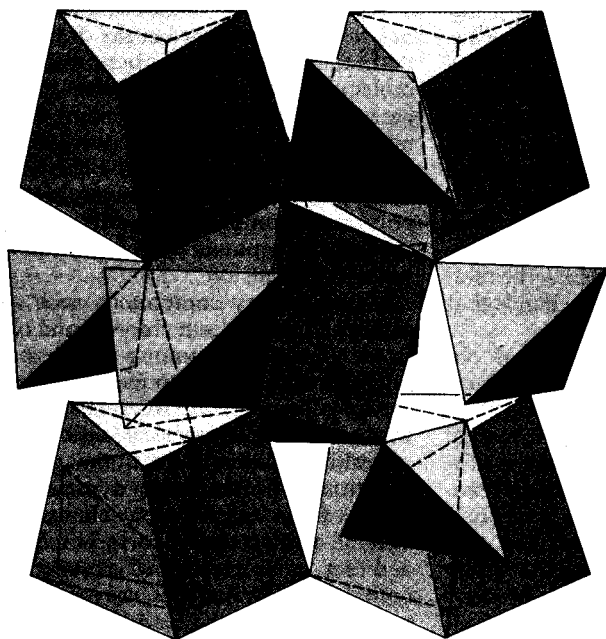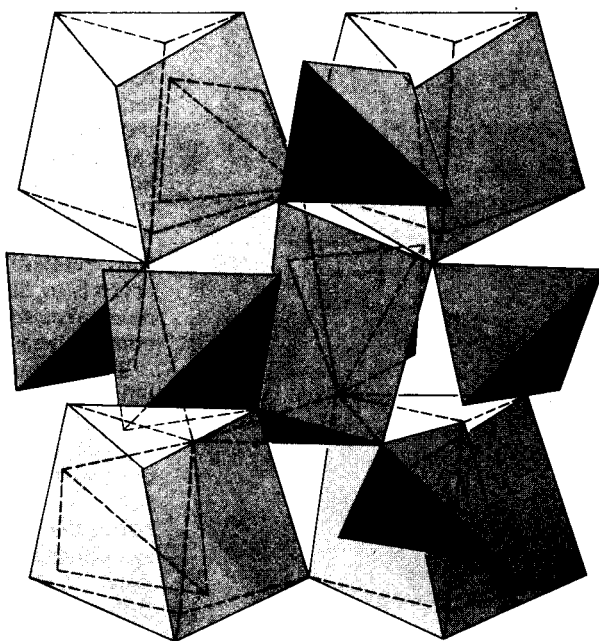

SODIUM IODATE (NaIO₄)
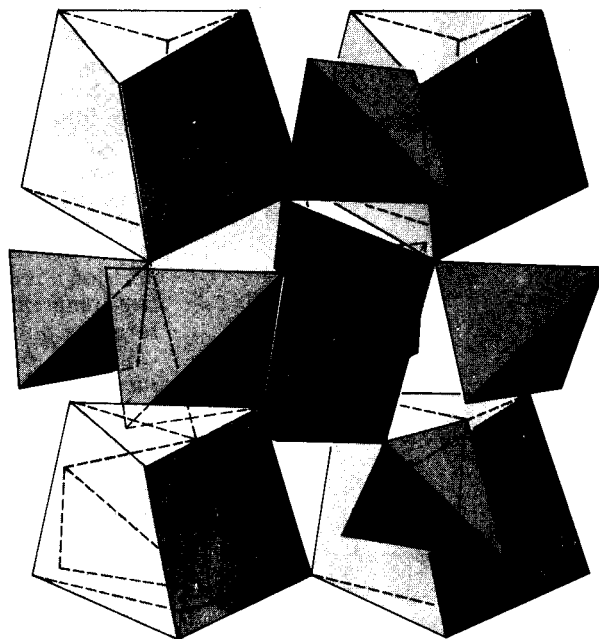
CALCIUM TUNGSTATE (CaWO₄)

BISMUTH VANADATE (BiVO₄)

ZIRCONIUM GERMANATE (ZrGeO₄)

SCHEELITE-TYPE COMPOUNDS, which have the general chemical formula ABO_4, are composed of two types of cation polyhedron. The small B tetrahedrons, shown in red, are comparatively incompressible and occupy only 5 percent of the volume of the crystal. The large A polyhedrons, which can be viewed as distorted cubes, form a continuous three-dimensional network and fill most of the crystal's volume. Thus the reduction in the volume of the crystal under increased pressure is determined predominantly by the com- **pression of the large eight-coordinated A polyhedrons. The four representative scheelites shown in this illustration are identical in crystal structure; the bulk crystals differ widely in compressibility, however, because of large differences in the compressibility of their constituent A polyhedrons. In this case the range of relative compressibility is indicated by a spectrum of colors: the red end of the spectrum designates the structure with the least compressible bonds and the violet end the structure with the most compressible bonds.**

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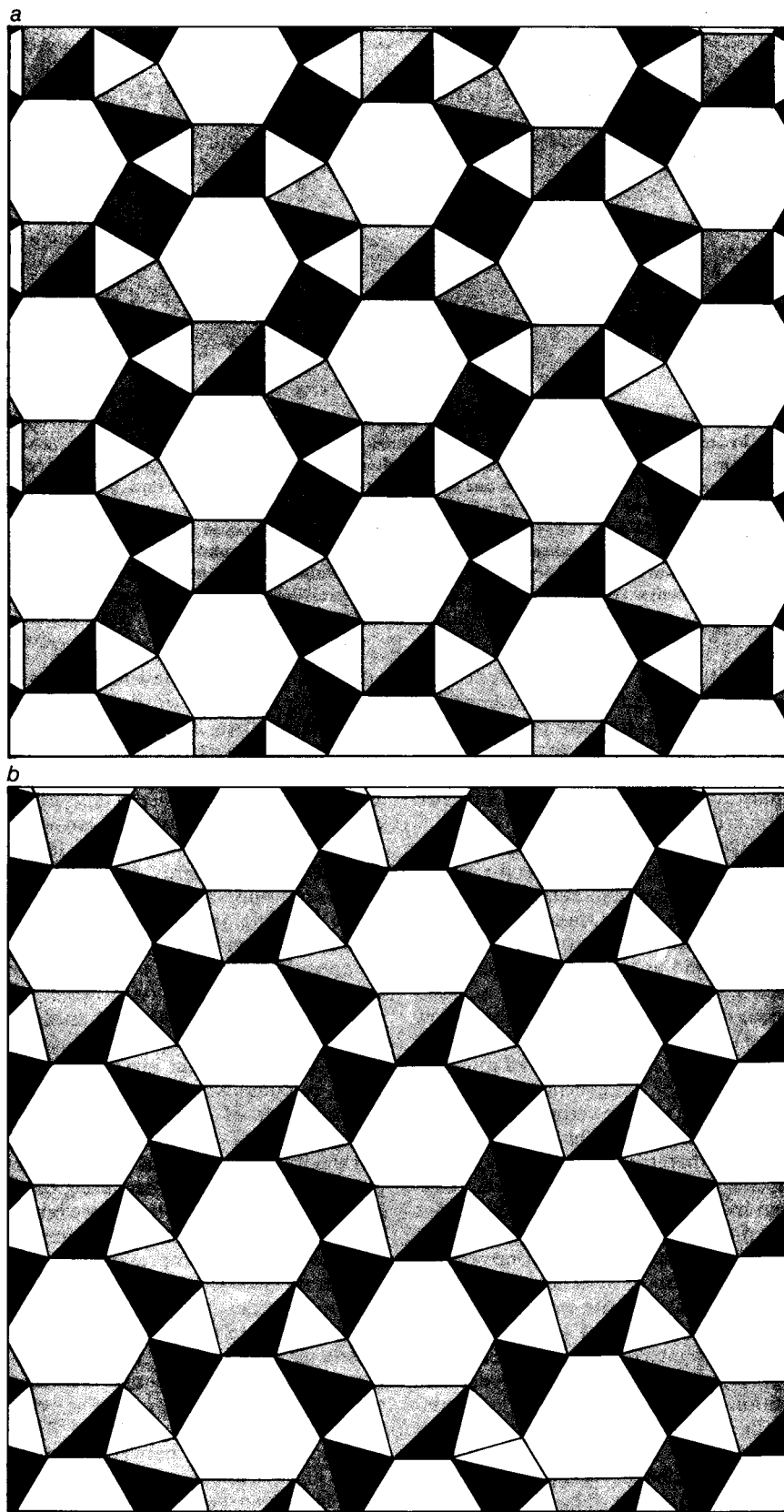
CRYSTAL STRUCTURE OF QUARTZ (SiO_2), the commonest oxide of silicon, consists of a complex, three-dimensional network of silicon-centered tetrahedrons, all of whose corners are shared (*a*). In quartz compression is attributable primarily to the bending of the bond angles between the polyhedrons (*b*). As a result a bulk crystal of quartz is 10 times more compressible than its constituent polyhedrons. Quartz serves as a counterexample to the intuitive notion that the hardest substances are the least compressible; because of its strong framework of silicon-oxygen bonds, quartz is one of the hardest compounds in nature, and yet it is one of the most compressible of the common rock-forming minerals.

uous three-dimensional framework. The small tetrahedrons with their highly charged cations are quite rigid, changing by less than 1 percent in volume even at pressures as high as tens of thousands of atmospheres. Nevertheless, quartz crystals are 10 times more compressible than their constituent polyhedrons, because the angles between the tetrahedrons are free to bend. The bending of the bond angles between the silicon and oxygen ions requires much less energy than the shortening of the bonds between the ions, and so the "tilting" of the polyhedrons becomes a more efficient compression mechanism.

In some compounds polyhedral tilting is responsible for a dramatic phase transition. For example, rhenium oxide (ReO_3) is composed of extremely incompressible octahedrons, each of which has a rhenium cation at the center surrounded by six oxygen anions [*see illustration on opposite page*]. At normal room temperature and pressure the crystal is cubically symmetrical; that is, all the octahedrons are constrained to align themselves along the axes of a cube. No tilting is possible in this cubic form of the crystal, and the oxide is correspondingly incompressible. At a pressure of about 5,000 atmospheres, however, a striking change takes place. The oxide undergoes a phase transition to a form with the same linkage of octahedrons but with a lower degree of symmetry; as a result the rhenium-oxygen clusters are free to tilt. At the transition point the compressibility of the crystal increases more than tenfold, simply because the dominant compression mechanism changes from bond shortening to bond-angle bending.

The greatest dimensional changes observed in crystals at high pressure are associated with intermolecular compression. The weak bonds between adjacent molecules may shorten by more than 1 percent per 1,000 atmospheres. Such a large effect dominates the behavior under compression of any material in which the bonding is molecular. The simplest condensed substances displaying molecular bonding are high-pressure crystals of elements that are gaseous at normal room conditions. The inert gases neon and argon, for example, can be liquefied at very low temperatures and then loaded into the gasket chamber of a diamond-anvil cell. The elemental fluids crystallize at high pressure, and even at room temperature they retain their crystalline form if they are confined at pressures of several thousand atmospheres. Hence it is possible to study the crystal structures and compressibilities of the crystalline phases.

X-ray-diffraction experiments reveal that at high pressure and room temperature crystals of neon and argon adopt the familiar cubic-close-packed structure, which is also characteristic of many metallic elements. The inert-gas crystals, however, have compressibilities unprecedented in magnitude; changes in volume of more than 1 percent per 1,000 atmospheres are observed in these materials, whereas the cubic-close-packed metals can be compressed by no more than about a tenth of this amount.

Gases consisting of multi-atom molecules can exhibit much the same behavior. For example, methane (CH_4) crystallizes at a pressure of about 16,000 atmospheres; the structure is also the cubic-close-packed arrangement, but the five-atom methane molecule rather than a single atom of neon or argon forms the close-packed unit. As in inert-gas crystals, the compressibility of crystallized methane is on the order of 1 percent per 1,000 atmospheres. A number of other multi-atom gases, including hydrogen (H_2), oxygen (O_2), nitrogen (N_2) and carbon dioxide (CO_2), also form extremely compressible molecular crystals at high pressure.

Crystals of pressurized gas are among the simplest to display molecular bonding, but they are by no means the only ones. Virtually all organic crystals, from solid forms of alcohols and hydrocarbons with a few tens of atoms per molecule to giant proteins with tens of thousands of atoms in each molecular unit, have highly compressible molecular bonds. It is easy to predict that all these substances will prove highly compressible compared with the inorganic minerals that form the solid earth. It is also easy to imagine the extreme anisotropic compression that must be displayed by some organic molecular crystals such as polymers, in which strong carbon-carbon bonds form continuous chains along one axis of the crystal and are joined laterally only by weak intermolecular forces.

Layered atomic structures exhibit fascinating and revealing behavior under compression. Layered compounds are anisotropic by definition; the bonding within each layer is stronger than the bonding between the layers. These differences in bond strength result in contrasts in compressibility along different crystal directions. Graphite, the commonest form of elemental carbon, is a classic example of a layered structure. Carbon-carbon bonding within each layer is as strong as that in diamond, and yet adjacent layers are bonded by molecular forces so weak
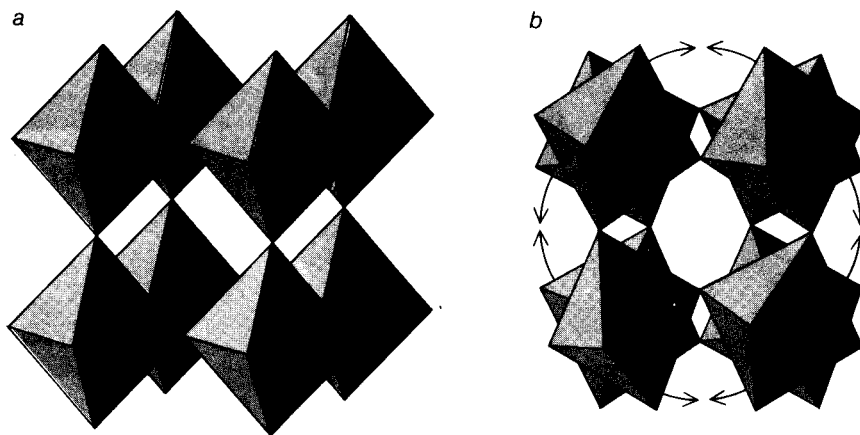
RHENIUM OXIDE (ReO_3) consists of a simple corner-linked array of rhenium-centered octahedrons. Each rhenium cation is positioned at the corner of a unit cube of the crystal structure, and the rhenium-oxygen bonds lie along the edges of the cube (a). Under normal room conditions the compound is one of the least compressible oxides known, because compression can occur only by shortening the rigid ionic bonds. At a pressure of about 5,000 atmospheres, however, rhenium oxide undergoes a phase transition to a structure with the same arrangement of octahedrons but with a lower degree of symmetry (b). The volume of the high-pressure form is reduced by the more favorable mechanism of bond-angle bending, or polyhedral tilting. At the transition the compressibility increases more than tenfold.

that graphite is valued as a lubricant. The contrast between the compressibility parallel to and perpendicular to the layers is also dramatic; compression between the layers is more than 50 times greater than compression within the layers.

Layered silicates, including such common mineral groups as the micas, talcs and clays, can respond to pressure by a combination of all three compression mechanisms: bond shortening, bond-angle bending and intermolecular compression. As a result these minerals reveal much about how pressure affects condensed matter.

One of the simplest layered minerals is brucite, or magnesium hydroxide [$Mg(OH)_2$]; it is the active ingredient in milk of magnesia. The main building block of this structure is an octahedron of magnesium coordinated to six oxygen-hydrogen pairs. The polyhedrons are linked by shared edges to form continuous layers that are one polyhedron thick. Slabs of octahedrons, each with the basic brucite composition, are stacked one on top of another and are linked by intermolecular forces. The compression of magnesium hydroxide within the octahedral layers is controlled by the shortening of magnesium-oxygen bonds and hence is similar to the linear compressibility of magnesium oxide. The compressibility perpendicular to the layers is many times greater.

Layered silicates are all composed of several polyhedral layers stacked in some regular sequence. An octahedral layer, like that of brucite, is a

ubiquitous feature of layered magnesium silicates; a layer of silicon tetrahedrons is another. The silicon tetrahedral sheet differs from the octahedral sheet in that all the polyhedral units share corners with adjacent units in the same layer. Even though the individual tetrahedrons are rigid, the layers themselves are highly compressible because of bond-angle bending. Bond-angle bending is also important because for a wide range of different compositions it allows the size of the tetrahedral layer to conform to the more constrained octahedral spacing. Accordingly micas, clays and other layered silicates occur in a remarkable range of compositions.

A number of layered silicates are composed entirely of octahedral and tetrahedral sheets. In the mineral serpentine, for example, alternating octahedral and tetrahedral layers are bonded together by intermolecular forces. The anisotropic compression of serpentine is similar to that of magnesium hydroxide: the compression is much greater in the direction of weak interlayer bonding. The most remarkable feature of this structure is related to bonding anisotropies. The two polyhedral layers are joined at flexible shared corners between octahedrons and tetrahedrons. Furthermore, each layer can bend. As a result serpentine layers can curve and form fibrous crystals in which the atomic layers are rolled up like a carpet. This fibrous form of serpentine, called chrysotile asbestos, has a layered atomic structure that is in distinct contrast to many other needlelike crystals,

in which long chains of atoms line up along the crystal axis. The crystal form, like the anisotropic compression, is a consequence of the great difference of bond strengths within and between polyhedral layers.

Talclike silicates are composed of one octahedral layer sandwiched between two tetrahedral sheets. Used for centuries in lubricants and as talcum powder, these common layered minerals provide another example of anisotropic properties that result from anisotropic bonding. Talc and serpentine display all three compression mechanisms. Magnesium-oxygen and silicon-oxygen bond shortening occur within the polyhedral sheets. Tetrahedral layers conform to the size of octahedral layers through changes in the silicon-oxygen bond angles. Intermolecular compression accounts for most of the reduction in volume perpendicular to the layers. Without recognizing
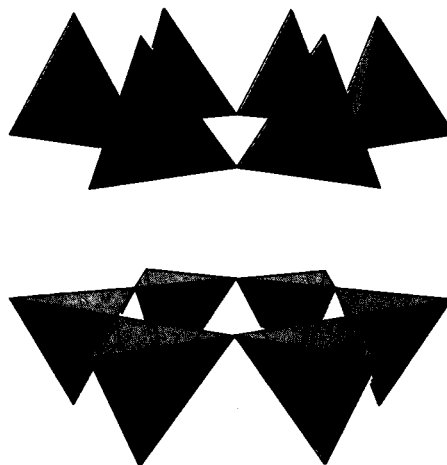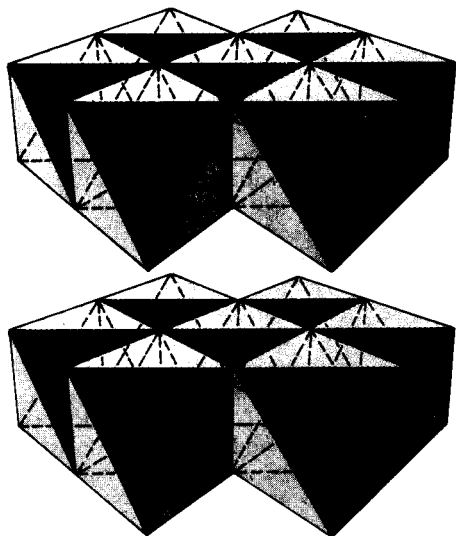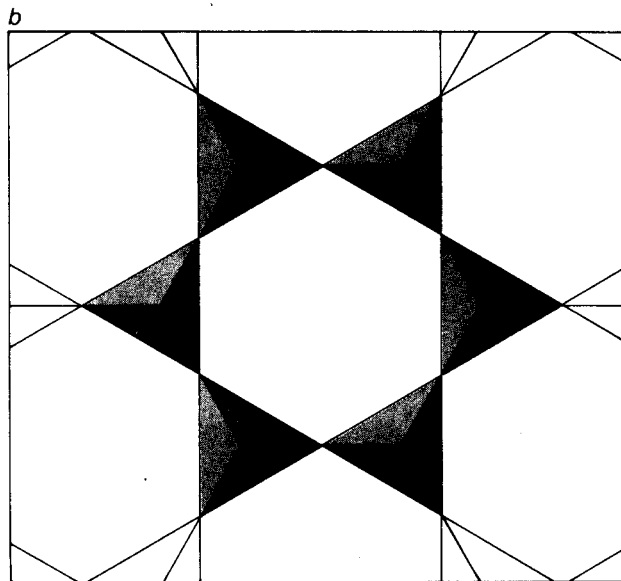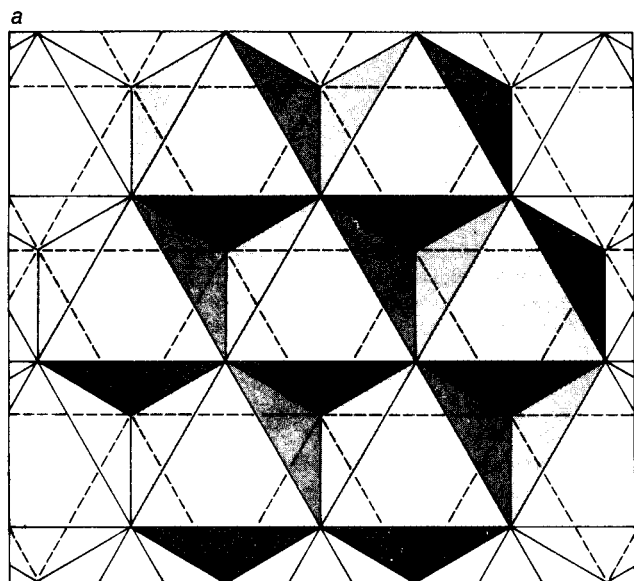
LAYERED SILICATES have a characteristic crystal structure that is based on the stacking of octahedral and tetrahedral sheets. The octahedral sheet viewed from the top and from the side in panel *a,* for example, is made up of a single layer of edge-sharing, cation-centered octahedrons. The simplest structure to incorporate this feature is the mineral brucite, or magnesium hydroxide [$Mg(OH)_2$], in which the octahedral layers are joined by weak molecular bonds. The compressibility of brucite within the layers is determined by the compressibility of the magnesium-oxygen bonds; the compressibility between the layers, however, is many times greater. In contrast, the polyhedral silicon dioxide sheet shown in panel *b* is composed of corner-linked silicon-centered tetrahedrons to form an infinite two-dimensional array of six-member rings. The compression of this layer is facilitated by bond-angle bending, which is energetically more favorable than the shortening of the rigid silicon-oxygen bonds. For example, the serpentine group of minerals is formed from the superposition of one such tetrahedral sheet onto one of the aforementioned octahedral sheets (*c*). In this structure some oxygen atoms are shared by both polyhedral layers. The double polyhedral sheets are also linked by intermolecular forces, which are so weak that many serpentines fail to form regular three-dimensional crystals. The individual layers often bend, curl or even roll up like a carpet to form long, needlelike crystals. In effect the two different polyhedral layers that make up the serpentine sheet behave like the bimetallic strip in a thermostat. One curious result is that the serpentine structure, which is basically planar, produces the most fibrous of all minerals: chrysotile asbestos (*bottom part of panel* c). Layered silicates such as talc, on the other hand, are composed of a stack of triple sheets, each of which consists of an octahedral layer sandwiched between two tetrahedral layers (*d*). Because of the symmetrical sequence of layers, talc is incapable of bending; that is what makes talcum powder a good lubricant. The compressibility of talc within the layers is equal to that of the octahedral layer, but the compressibility between the layers is several times greater.

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each of these three common mechanisms of crystal compression, it is not possible to understand or describe the response of these structures and others to high pressure.

In sum, the polyhedral approach enhances understanding of crystal compression and other crystal properties by establishing correlations between atomic-scale interactions and macroscopic crystal behavior. The approach is empirical in the sense that it is based on experimental data rather than on theoretical predictions. It is complementary to more rigorous quantum-chemical methods, which can lead to calculations of crystal properties from first principles but which are not yet applicable to the multi-atom structures found in nature. The polyhedral approach therefore greatly facilitates efforts to understand crystal compression and other phenomena in the real world.

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